N O T I C E

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ELEMENTS OF THE THEORY OF MOLECULAR SPECTRA

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FOREWARD

In this paper we present the basic aspects of the theory /2*
concerning the spectra of multiatomic molecules: the classifi-
cation of the forms of motions in a molecule, the methods for
determining the corresponding Schroudinger levels, the spectral
types and the selection rules. The paper is intended for a wide
circle of astrophysicists who are interested in the spectral
properties of molecules so as to identify their presence and
state in outer space.

INTRODUCTION /3

In recent years a whole series of molecules have been dis-
covered in outer space, including multiatomic molecules. There
is reliable evidence that such molecules as formaldehyde, ammonia,
methylacetylene, acetaldehyde, methyl alcohol, etc. exist there.
At present more than 20 molecules and molecular ions all told
are known which are found in outer space. In this connection
the interest of astrophysicists in these formations which are
new to them is understandable.

The search for molecular formations in space and their inter-
pretation, their identification is carried out by means of spec-
tra. Basically these spectra are recorded at present in the
radio-frequency range, but obviously in subsequent stages both
radiation and absorption in the infrared, as well as in the ultra-
violet regions of the spectrum will be used to record and identify
molecules. In other words, research will be conducted in all
ranges where molecular spectra appear.

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*Numbers in the margin indicate pagination of original foreign text.

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A molecule is a system which is significantly more complex than an atom. Along with the motions of the electrons, there exist in molecules relative motions of the nuclei inside the molecule (vibratory motions), as well as the motions of the entire molecule as a whole (rotary motions)*. As a result, molecular spectra possess significantly greater variety than atomic spectra. Consequently the interpretation of molecular spectra and their theoretical calculation become problems which are incomparably more complex than the problem of calculating and interpreting atomic spectra.

The purpose of the present lecture is to give a brief resume of the basic aspects of the theory which deals with the moleculare spectra of multiatomic molecules and to indicate the computational approaches which can be used to study the molecular spectra of multiatomic molecules in order to interpret them and to analyze possible changes in the spectra due to various kinds of influences on a molecule. Naturally, the brevity of the lecture does not allow us to dwell on many important subtile questions in the theory of molecular spectra; therefore we shall restrict ourselves to a discussion of the most fundamental theoretical aspects of the subject.

At first glance it may appear that the "astrophysicist-molecularist" hardly ever encounters problems involving a detailed study and, a fortiori, the calculation of a molecular spectrum. Indeed, if a molecule is in a basic state in an approximations thereto, then its spectral identification can be carried out by means of a chart or by a more complex approach based on a so-called artificial intelligence. The development of special automated systems for identifying molecules by means of their spectra has now become one of the most intensely developing trends in instrumental analytic chemistry, or more precisely, analytic physics. The reader can acquaint himself with some of

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*Translational movements are of no interest to us.

the most important aspects of this branch of science by consulting the review [1]. However, it is clear, a fortiori, that under the conditions of outer space, where molecules are subjected to the influence of quite powerful ultraviolet radiation and X-rays, molecules can be found in the most varied states, including those /5 that are highly ionized. Here the problem of identifying them spectrally is extremely complicated and can rarely be done without a detailed theoretical analysis of the possible spectral transitions between the energy levels of the "suspected" molecule or ion. It is precisely for this reason that the contemporary astrophysicist is obliged to know at least the basics of the theory of molecular spectra. The reader who wishes to acquire a more profound knowledge of this theory may consult the monographs [2-6].

1. Classification of Molecular Motions; the Equations for Electron, Vibratory and Rotational Spectra

As is well known, in order to define and study the energy levels of any complex system, it is necessary to formulate and solve the appropriate Schroedinger equation. In the case of multiatomic molecules this equation can be written as follows:

$$\left(\hat{T}_\ni(q) + \hat{T}_\mathfrak{a}(Q) + V_{\ni\mathfrak{a}}(q,Q) + V_{\mathfrak{a}\mathfrak{a}}(Q) + V_{\ni\ni}(q)\right)\Psi(q,Q) = E_{\ni\mathfrak{a}}\,\Psi(q,Q), \quad (1)$$
(1)

Here $\hat{T}_\ni = T_\ni(q)$ is the operator which expresses the kinetic energy of the electrons;

$\hat{T}_\mathfrak{a} = \hat{T}_\mathfrak{a}(Q)$ is the kinetic energy operator of the nuclei of the molecules;

$V_{\ni\mathfrak{a}} = V_{\ni\mathfrak{a}}(q,Q)$ is the operator for the Coulomb attraction between the electrons and the nuclei, or the operator of the electron-nucleus interaction;

$V_{я я} = V_{я я}(Q)$ is the operator of the Coulomb repulsion between the nuclei, or the operator of the nuclear inter- action;

$V_{э э} = V_{э э}(q)$ is the operator of the Coulomb repulsion between the electrons, or the electron-electron interaction;

q and Q are respectively the election and nuclear coordinates.

In this form the equation is called the Coulomb approximation equation. More complex interactions such as the electron-orbital effects, spin effects, etc., can only be taken into account in the higher approximations of the contemporary spectrum theory of multiatom molecules, since they lead to small corrections and correspondingly to very small changes in the spectra which are difficult to record experimentally as a rule.

The Schroedinger equation in the form (1) cannot be solved exactly and therefore in order to obtain information about the energy levels in multiatom systems it is necessary to make a whole series of supplementary assumptions and to apply the technique of approximate calculations which is based principally on various versions of variational methods.

The basic approximation which is used to calculate the energy levels corresponding to the movements of electrons is the so-called adiabatic approximation. The ability to use this approximation is based on the fact that the operator of the kinetic energy of the electrons and the nuclei contains the opposite masses of the electrons and the nuclei. Since the masses of the nuclei exceed the mass of the electrons many times over, the intrinsic equation describing the purely electronic movements can be obtained if it is assumed as a first step that

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the masses of the atoms are infinitely heavy relative to the
electron masses.

In this case the operator of the kinetic energy of the nuclei
in (1) can be entirely omitted, and the energy contributed by
the nuclei-nuclei repulsion is simply considered as an addi-
tion to the energy of the purely electron movement. In this
case the problem becomes a problem concerning the movement of
·electrons in a field of immoble nuclei. The corresponding equa-
tion for this problem is:

$$\left(\hat{T}_{\ni}(q) + V_{\ni\jmath}(q) + V_{\ni\ni}(q) - V_{\jmath\jmath} \right) \Psi_{\ni}(q) = E_{\ni} \Psi_{\ni}(q).$$ (2)

On solving this equation, we obtain the values of the
energy levels which correspond to the purely electron movement,
or, as one says, the value of the electron energy levels. If
we select some fixed arrangement of the electrons relative to
each other, then to this fixed position of the nuclei there will
correspond its own set of electron energy levels. If the rela-
tive arrangement of the nuclei is changed, then we obtain a
new problem concerning the electron energy level. On solving it,
we find a new set of values of the energy levels.

If a molecule is deformed over a sufficiently wide interval,
then each value of the energy level is a function of the mutual
arrangement of the nuclei, and will depend on the parameters
just as on the coordinates which describe the arrangement of the
nuclei relative to each other. Since these very same coordinates
can be used to describe the purely vibratory movements, we shall
henceforth say that each electron energy level is a parametric
function of the vibratory coordinates. Each value of the electron
energy $E_{m\ni}(Q)$ $(m = 1, 2, 3 \ldots)$ will be stored on some smooth surface
called a <u>potential surface</u> of the molecule. There will be as
many surfaces (in the case of the two-atom molecules -- potential
curves) as there are values $E_{m\ni}(Q)$. The potential surfaces

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of multiatom molecules are extremely varied. The form of these
surfaces is essential to an understanding of the nature of mole-
cular spectra and therefore it is useful to give at least a
rough classification after we have distinguished their possible
forms as follows.

1. Potential surfaces with a single minimum.

For the one-dimensional case or section such a potential
surface is shown schematically in Fig. 1a. This potential sur-
face is characteristic of many molecules, especially in the so-
called basic or equilibrium configurations. The minimum energy
value corresponding to such a surface represents the energy of
a molecule in the basic state, and the set of relative coordin-
ates of the nuclei corresponds to the equilibrium configuration
of the molecule. Molecules which are in states with a single
minimum have a clearly expressed geometric form. After computing
the position of this minumum as a function of the relative co-
ordinates of the nuclei we can find the equilibrium geometric
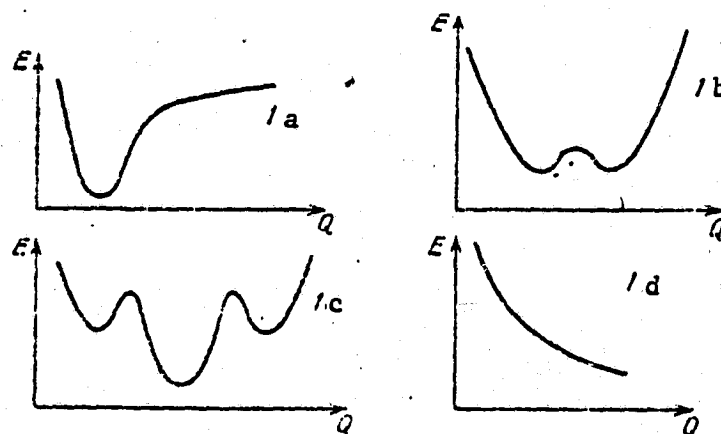configuration of the molecule and, consequently its form.

Fig. 1. Schematic representations of the potential
curves or sections of potential surfaces.

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2. Potential surfaces with two or more minima.

Often situations are encountered in which the potential surface has two or more minima along one or several coordinate axes (cf. Fig. 1b, c). This occurs, e.g., in the ammonia molecule in the case of the coordinate corresponding to the movement of the nitrogen atom shown in Fig. 2.
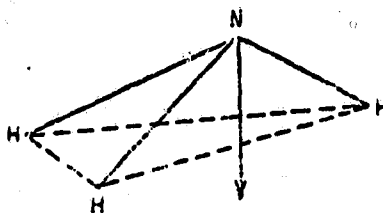
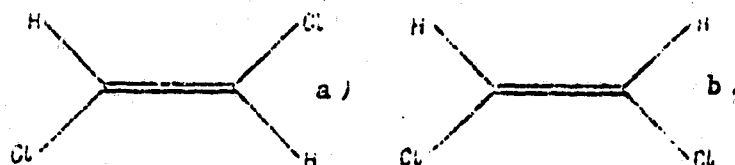Fig. 2. Inversion movement (shown by the arrow) of the nitrogen atom in an ammonia molecule.

Fig. 3. Trans- (a) and cis- (b) isomers of a molecule of di-chlorethylene.

The nitrogen atom with the highest probability is arranged either above or below the plane of the three hydrogen atoms. When it has attained a sufficiently large amplitude this atom may "cut through" this plane and go over into a lower state. The potential curve representing this movement has the form shown in Fig. 1b.

The existence of such potential surfaces with two minima leads
to a characteristic phenomenon in spectra which is called in-
version doubling.

Surfaces with two minima arise when so-called cis- and
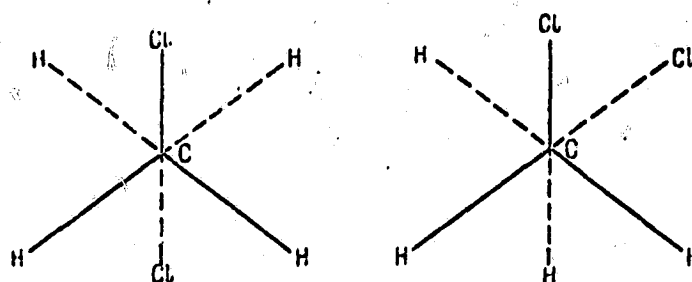trans-isometry occurs. Examples of this type of isometry are
shown in Fig. 3.

Fig. 4. Rotational isomers of a molecule of di-
chlorethane (view along the C-C bond).

As a rule, the transition of a cis-isomer into a trans-
isomer requires a significant amount of energy. Therefore the
potential barrier separating the two molecular states turns out
to be so high that we may speak of the existence of two different
molecules (respectively the cis- and trans-isomers). Potential
surfaces with many minima are encountered when there is so-called
rotational isometry.

An example of rotational isometry corresponding to the
potential curve in Fig. 1c is shown in Fig. 4.

If the potential barrier separating different possible sur-
face configurations of molecules is sufficiently high and broad,
then we may speak of several different molecules corresponding
to different rotational isomers, and when analyzing their spectra,
simply consider each of these possible isomers individually.

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If however, as is often the case, the potential barrier separating individual isomeric forms is not very large, then such an approach is incorrect and it is necessary to solve the problem, taking into account the multi-minima property of the potential surface. The presence of several minima in this case may lead to the appearance of a number of energy levels which differ very little from each other. In individual cases these levels are situated so near one another that in the spectrum they do not appear individually, but only an expansion of the absorption /11 or radiation bands is observed.

3. The third characteristic type of potential surface comprises surfaces which have neither a single minimum nor very deep minima (cf. Fig. 1d). Such surfaces correspond to unstable molecular states. This type of surface results in the appearance of discontinuous spectra.

4. Finally, the fourth type of potential surface is a surface which has gullies of either extended or annular form. These surfaces arise when there is degeneracy of the electron state, and they also result in the appearance of definite peculiarities in the electron and vibratory spectra of multiatom molecules. When a sufficiently prolonged gully is present relative to certain coordinates, the concept of the form of the molecule may become meaningless.

To solve the Schroedinger equation for the movement of electrons is an extremely complicated problem, and the solution cannot be expressed in analytic form.

However, there are specific methods for obtaining approximate solutions to this equation. Later we shall give a brief characterization of these methods. For the present we shall only show that, although the result is merely approximate, nevertheless, by means of the contemporary theory of electron shells it

is possible in the case of multiatom molecules to calculate numerically both the parameters of the potential surfaces of molecules as well as the energy levels to a degree of precision which is sufficient in many cases to interpret reliably at least the basic absorption and radiation bands in the spectra of molecules which sometimes contain tens of atoms. This especially concerns systems which possess so-called <u>conjugate bonds</u>. Among such systems are the molecules of benzene, naphthalene, anthracine, compounds of the diene type, etc.

If we know the solution (the energy values and the eigen-functions) of equation (2), then it is natural to seek the solution of (1) in the form:

$$\Psi_{\mathfrak{I}\mathfrak{L}}(q,Q) = \Psi_{\mathfrak{I}}(q,Q)\,\Psi_{\mathfrak{L}}(Q) \tag{3}$$

Here and below we shall assume that all the eigen-functions are real. The symbol Q and the notation $\Psi_{\mathfrak{I}}(q,Q)$ emphasize the parametric dependence of this function on the nuclear coordinates.

Let us substitute (3) into the expression for the mean value of the Hamiltonian of (1):

$$\bar{H} = \int \Psi_{\mathfrak{I}}(q,Q)\,\Psi_{\mathfrak{L}}(Q)\,[\hat{T}_{\mathfrak{L}} + \hat{H}_{\mathfrak{I}}]\,\Psi_{\mathfrak{I}}(q,Q)\,\Psi_{\mathfrak{L}}(Q)\,dq\,dQ \tag{4}$$

Here

$$\hat{H}_{\mathfrak{I}} = \hat{T}_{\mathfrak{I}} + V_{\mathfrak{I}\mathfrak{I}} + V_{\mathfrak{I}\mathfrak{L}} + V_{\mathfrak{L}\mathfrak{L}} \tag{5}$$

Integrating in (4) with respect to the electron coordinates, and taking into account the orthonormalization of the functions and assuming that the function $\Psi_{\mathfrak{I}}(q,Q)$ depends weakly on the nuclear coordinates (this is correct in the absence of electron

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degeneracy), so that we may neglect the effect of the differential operator $\hat{T}_{\mathfrak{A}}$ on this function, we obtain

$$\bar{H} = \int \Psi_{\mathfrak{A}}^0(Q)\left[\hat{T}_{\mathfrak{A}} + E_{\mathfrak{s}}(Q)\right]\Psi_{\mathfrak{A}}^0(Q)\,dQ .$$

(6)

(recall that $E_{\mathfrak{s}}$ depends parametrically on the nuclear coordinates).

Selecting some origin of reference (usually the minimum point of the potential surface is chosen), we represent $E_{\mathfrak{s}}(Q)$ in the form

$$E_{\mathfrak{s}}(Q) = E_{\mathfrak{s}}(0) + \Delta E_{\mathfrak{s}}(Q)$$

Then $\bar{H} = E_{\mathfrak{s}}(0) - \bar{H}$,

(7)

where

$$\bar{H}_{\mathfrak{A}} = \bar{T}_{\mathfrak{A}} + \Delta E .$$

Thus we may conclude that the intrinsic equation for nuclear /13 motions must be

$$\left[\hat{T}_{\mathfrak{A}}(Q) + \Delta E_{\mathfrak{s}}(Q)\right]\Psi_{\mathfrak{A}}^0(Q) = E_{\mathfrak{A}}\,\Psi_{\mathfrak{A}}^0(Q).$$

(8)

This treatment conforms to the adiabatic approximation in which it is possible to separate the electron and nuclear motions. The values of the energy levels are then calculated by means of the formula: $\quad E_{\mathfrak{s}\mathfrak{A}} = E_{\mathfrak{s}}(0) + E_{\mathfrak{A}}$

(9)

The role of the potential energy in equation (8) is filled by the term $\Delta E_{\vartheta}(Q)$, which represents the increment in the mean value of the total electron energy in comparison to the initial value, taking into account the nucleus-nucleus repulsion. The quantities $\Delta E_{\vartheta}(Q)$ and E_{ϑ} are calculated for each electron state. Consequently, in order to investigate completely the nuclear movements, it is necessary to solve a large number of equations of the type (8) with different potential functions corresponding to the potential surfaces.

In order to separate the electron and nuclear variables, we must introduce supplementary assumptions. A precise solution of the problem can be obtained if we construct a wave function in the form of linear combinations of adiabatic wave functions. This involves computing the various kinds of matrix elements of the electron-nucleus interaction and solving homogeneous algebraic equations. Generally speaking, this does not present any basic difficulties, but it is a very laborious problem. In ordinary theoretical calculations of spectra such operations are not performed. Corrections for nonadiabaticity become essential only when the potential surfaces of two or more electron states come together. Ordinarily this occurs only at individual points which as a rule are remote from a minimum. In this case electron degeneracy arises and the corrections due to the energy of the nuclear motions are not small in comparison with the distance between the energy levels corresponding to the purely electron motions. The nuclear motion removes this degeneracy and results in specific effects. One of the most interesting of these is the Jahn-Teller effect [7].

We shall consider only those cases in which we can confine ourselves to the adiabatic approximation. Then the nuclear motion can be described by the Schroedinger equation of type (8). The potential part of this equation depends obviously only on the change in the relative arrangement of the nuclei. If the entire system of nuclei is translated or rotated, then the potential

part should not vary here. Therefore a further simplification of the equations can be achieved if we introduce a suitable system of coordinates which describe individually the relative motions of the nuclei (or their oscillations) and the rotation and the translational motion of a molecule as a whole. The kinetic energy operator of the nuclei for a multiatomic molecule has the following form in an aribtrary system of curvilinear coordinates:

$$\hat{T}_{\mathfrak{q}} = -\frac{\hbar}{2}\sum_{k,n} |T|^{1/2} \frac{\partial}{\partial Q_k}\left(\frac{\tau_{kn}}{|T|^{1/2}} \frac{\partial}{\partial Q_n}\right). \tag{10}$$

Here the τ_{kn} are the elements of the so-called matrix of the kinematic coefficients (T);

$|T|$ is the determinant of this matrix.

The matrix of the kinematic coefficients contains the elements written in the selected curvilinear coordinates, which are included in the classical expression for the kinetic energy of a set of material points. As well known, this expression is /15 given by a quadratic form:

$$T_{кин} = \frac{1}{2}\sum_{k,n} \tau_{kn} P_k P_n,$$

where P_k are the pulses conjugate to the chosen vibrational coordinates (describing the deformations of the molecule), the rotational and translational coordinates. The latter are invoked to characterize the motions of the molecule as a whole.

The elements τ_{kn} form a square symmetric matrix and in the general case they themsleves depend on the curvilinear (in particular, the vibrational) coordinates.

Mathematically the separation of the variables (the vibrational, rotational and translational) is connected with the transformation of coordinates under which the matrix T is reduced to block form.

If the isolation of the translational motions can be carried out in the simplest fashion, then the separation of the vibrational and rotational motions cannot be performed precisely in the case of a multiatom molecule. One of the reasons for this is that the very concept of the rotation of a system is not completely defined in this case if the system itself is deformed in the process of rotation.

Indeed, if we are dealing with a solid body, then in this case its position in space can be characterized by specifying the angles between the directions of the principal moments of inertia and the axes of the external system of coordinates or the Euler angles. In a solid body the directions of these principal moments of inertia are fixed relative to the body itself. If, however, the body is not solid, but similar to a molecule in the state of performing vibratory (relative) movements, then the values of the principal moments of inertia vary /16 over time both due to the fact that the body rotates in space as a whole, as well as because it is deformed. Only in the two-atom molecule is the location of the axis of the molecule independent of its deformation, and in this case the isolation of the oscillations from the rotations can be carried out completely. In the multiatom molecule such an approach not connected with the oscillations cannot be introduced successfully and therefore the separation of the oscillations from the rotations can be performed only approximately. We cannot dwell on this important and interesting question and we refer the reader to the special literature [8].

Let us assume, however, that such a separation has been carried out. In this case the kinetic energy operator for the

nuclear motion can be represented in the form:

$$\hat{T}_{\mathfrak{a}} = \hat{T}_{k} + \hat{T}_{\delta}$$

Accordingly the equations for the vibrational and rotational motions separate out and have the form:

$$\left(\hat{T}_{k} + \Delta E_{\mathfrak{a}}\right) \Psi_{k} = E_{k} \Psi_{k} \tag{11}$$

$$\hat{T}_{\delta} \Psi_{\delta} = E_{\delta} \Psi_{\delta} \tag{12}$$

The coefficients contained in the equation for the rotational motion depend parametrically in the general case on the coordinates describing the deformation of the molecule. Therefore, generally speaking, the equations (12) must be solved for the different oscillatory states of the molecule. Only in a specific approximation can this be omitted.

Finally, the complete wave functions of the molecule in the adiabatic approximation and in the approximation to the complete separation of the oscillations and rotations can be written in the following form:

$$\Psi = \Psi_{\mathfrak{a}} \Psi_{k} \Psi_{\delta} \tag{13}$$

Accordingly the total energy of the system can be represented in the form:

$$E = E_{\mathfrak{a}} + E_{k} + E_{\delta} , \tag{14}$$

where E_{k} and E_{δ} are respectively the eigen-values of equations (11) and (12).

Therefore the system of levels of a multiatom molecule can be represented schematically as follows (cf. Fig. 5). During the interaction of an electromagnetic wave with the molecule, or if the molecule is in a disturbed state, then various transitions between energy levels can occur (cf. Fig. 5), resulting in the appearance of radiation or absorption spectra.
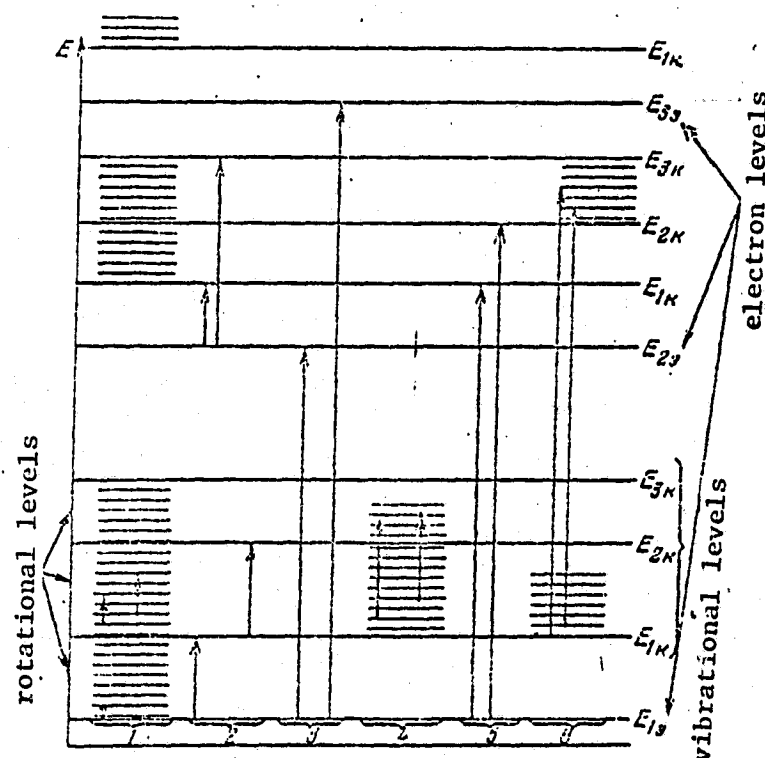

Fig. 5. Scheme of the levels and possible transitions (of spectra) in a multiatom molecule.

1 - purely rotational transition;

2 - purely vibrational transitions;

3 - purely electron transitions;

4 - vibrational-rotational transitions;

5 - electron-vibrational transitions;

6 - electron-vibrational-rotational transitions;

Since the system of levels turns out to be extremely rich, then naturally, the spectra of molecules also turns out to be extremely varied.

Let us give the characteristics of the basic types of molecular spectra.

2. The Types of Molecular Spectra

If the transitions between the rotational levels of the same electron and vibrational states are completed, then the so-called purely rotational spectra appear (cf. Fig. 5). The electromagnetic radiation or absorption related to these spectra correspond to the remote infrared or the microwave radio region.

If the transitions between the vibrational levels of the same electron state are completed, then there arise purely vibrational spectra (cf. Fig. 5). The radiation or absorption frequencies corresponding to these spectra lie in the near or the medium infrared region (the corresponding wave lengths occupy a range of approximately 2 to 100 microns). As a rule, however, along with the purely vibrational movements, rotational movements also build up, or the transitions between the rotational energy levels which are close to the given vibrational energy level are completed. Therefore the vibrational-rotational spectrum appears and the so-called rotational structure of the vibrational absorption or radiation bands is observed. An example of such a spectrum is shown in Fig. 6.
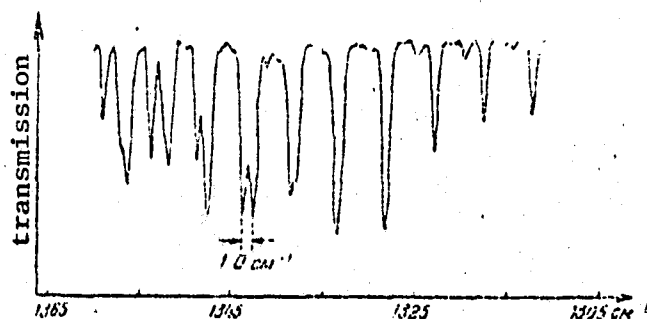
Fig. 6. A vibrational-rotational absorption band of a molecule of methane in the 1340 cm^{-1} region.

If the transition between the various electron energy levels is completed (cf. Fig. 5), then, as a rule, transitions are observed simultaneously between the vibrational and rotational states corresponding to the different electron levels. Spectra appear which are called electron-vibrational-rotational spectra.

Since the rotational energy levels in complex molecules are crowded very close to each other, the individual rotational transitions are often not observed. Blurs are obtained. Often, especially in large molecules, which turn out to have many vibrational levels that are often located in the spectrum, the individual transitions represented in Fig. 5 also do not appear, and as a result, broad, diffuse radiation or absorption bands are formed. An example of the corresponding spectrum is shown in Fig. 7.

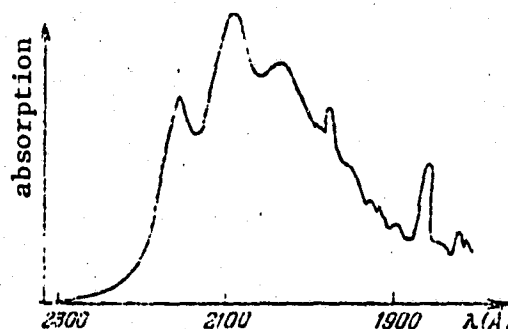Such are the basic features of the various kinds of molecular spectra.

Fig. 7. The electron absorption band
of a butadiene molecule.

Let us now turn to the solution of the Schroedinger equa-
tion for electron, vibrational and rotational motions.

3. Solution of the Molecular Equations.

1. The electron equation.

The Schroudinger equation for electron motions has no exact
analytic solution. Even the problem of the movement of a single
electron in a field of many centers is indeterminate. In a real
molecule there are many electrons, all of which interact with
each other. This, of course, substantially complicates the
problem.

The entire space in which electrons may move can be roughly
divided into two parts: the first, which comprises the space
between the nuclei as well as that close to them; and the second,
which is the peripheral space. In the peripheral region the
action of the nuclei is reminiscent of the action of a concen-
trated charge and the electron orbits take on the features of
atomic orbits. The so-called Rydberg series of electron states

is ained, and the total removal of an electron, i.e., the ionization limit for a molecule corresponds to the limiting case of an electron transition. In a good approximation the energies of the Rydberg states can be represented by the Rydberg formula:

$$E_m = A - \frac{R}{(m - \delta)^2}$$

where   A   is the ionization limit of the molecule;

R   is the Rydberg constant;

m   is the principal quantum number;

δ is the Rydberg correction which assumes values
for different molecules lying in the interval from
0.1 to 1.2.

The circumstances are significantly more complicated in the case of the inter- and near-nuclear region.

In this region the electrons move in a very complicated field of nuclear attraction. It is impossible to obtain an even approximately analytical expression for the energy levels and the eigen-functions in the general case. Only certain states of linear and plane aromatic molecules with a developed conjugate constitute an exception. Here we may use models of free electrons in potential containers of different forms as qualitative characteristics (the so-called metallic models).

The general principles for solving the electron problem are as follows. If at the first stage we neglect the interaction of the electrons with each other, then the problem of the motion of electrons is similar to the problem of an atom with a single electron. There is one difference, however. The present problem is solved for a field with many centers. The Hamiltonian of this

problem, $\hat{H}_j^{(0)}$ is given by $\hat{H}_j^{(0)} = \hat{T}_j + \hat{V}$. The correspond-
ing solutions can be found by the variational method from the
extremum condition for the total electron energy in the field
of the nuclei, after selecting an appropriate sample function
(molecular orbital). A linear combination of the atomic orbi-
tals (abbreviation: MO LCAO) which has the form

$$\varphi = \sum_k c_k \chi_k$$

(14)

is used for this purpose. Here the coefficients c_k are certain /22
variational parameters which are subject to determination on the
basis of the variational method.

The functions X_k are non-variational functions; for this
purpose somewhat simplified atomic hydrogen-like functions are
usually assumed which correspond to the basic electron state of
each of the atoms entering into the compsoition of the molecule.
Each function X_k or atomic orbital is centered on the corres-
ponding nucleus. Thus the molecular orbital is constructed
as a function defined on the entire space of the molecule being
studied.

The mean value of the operator $\bar{H}^{(0)}$ in (14) equals the
quadratic form $\bar{H}_j^{(0)} = \sum_{k,n} c_k c_n h_{kn}$ with elements

$$h_{kn} = \int \chi_k \hat{H}_j^{(0)} \chi_n \, dq$$. The external values of this quadratic
form are found exactly by means of the supplementary requirement
of orthonormality imposed on the functions (on the ellipsoid

$$S = \sum_{k,n} c_k c_n S_{kn} = 1, \qquad S_{kn} = \int \chi_k \chi_n \, dq$$) and they are the
approximate eigen-values of the Schroudinger equation with the
operator $\hat{H}_j^{(0)}$. Thus the matter reduces to the calculation
of the matrix elements h_{kn} and S_{kn} and finding the eigen-numbers
and vectors of the pair of quadratic forms $\bar{H}_j^{(0)}$ and S.

To each eigen-number $E_m^{(o)}$ there corresponds it orbital

$$\varphi_m^{(0)} = \sum_k c_k^{(m)} \chi_k,$$, where the $c_k^{(m)}$ are the elements
of the corresponding eigen-vector. It is immediately evident
that since the number of the coefficients "C" in the linear com-
binations of the atomic orbitals is finite, then as a result,
on solving the corresponding Schroudinger equation by means of
this procedure we shall find a finite set of energy levels,
whereas, generally speaking to this equation there corresponds
an infinite number of energy levels. Therefore the energy of
the basic electron state and that of a number of nearby states
are usually calculated. The states corresponding to highly
excited levels have not, as a rule, been successfully determined
with satisfactory precision by means of such a scheme.

The functions $\varphi_m^{(0)}$ characterize the spatial states of the
electrons. In the case of the characteristics of the spin
states the functions $\varphi_m^{(o)}$, dominate the spin components α and β
(corresponding to the projections of the spin +1/2 and -1/2).
This yields the so-called spin-orbitals. Henceforth we shall
always assume that the molecular orbitals are spin-orbitals.
Such a simple representation of the spin-orbitals is possible
if we neglect the spin-orbital interaction, as is usually the
case.

If there are many electrons in the system, then it is nec-
essary to arrange them with respect to the spin-orbitals in
accordance with the Pauli principle which assigns to each of them
its own number. Each possible arrangement of the electrons
with respect to the spin-orbitals corresponds to one of the
possible electron configurations. The energy of such a configura-
tion is $E = \sum_m E_m^{(o)}$ and the eigen-function $\Psi = \prod_m \varphi_m^{(o)}$, where
the summation is over all the spin-orbitals. We must take into
account the fact that the spin-orbitals which differ only in their
spin components have the same energy.

The electron configurations which differ from each other only in the number of electrons filling the spin-orbitals evidently possess the same energy. Thus each state with the eigen-function $\Psi = \prod_m \varphi_m^{(0)}$ is $(N!)$ -fold degenerate in accordance with the number of different arrangements of "N" electrons with respect to "N" spin-orbitals. The general expression for the electron eigen-function must then be sought in the form of a linear combination of expressions of the type $\prod_m \varphi_m^{(0)}$ with different arrangements of the electrons with respect to the spin-orbitals.

The reasons connected with the Pauli principle and the antisymmetry of the electron function relative to the transposition of any pair of electrons lead to an eigen-function in the form of the Slater determinant

$$\Phi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_1^{(0)}(1) & \varphi_1^{(0)}(2) & \cdots & \varphi_1^{(0)}(N) \\ \varphi_2^{(0)}(1) & \varphi_2^{(0)}(2) & \cdots & \varphi_2^{(0)}(N) \\ \varphi_3^{(0)}(1) & \varphi_3^{(0)}(2) & \cdots & \varphi_3^{(0)}(N) \\ \cdots & \cdots & \cdots & \cdots \\ \varphi_N^{(0)}(1) & \varphi_N^{(0)}(2) & \cdots & \varphi_N^{(0)}(N) \end{vmatrix} . \tag{15}$$

In this determinant the function $\varphi_k^{(0)}$ is one of the "N" spin-orbitals occupied in the given electron configuration. In parentheses the numbers of the electrons are shown which are in the spin-orbitals.

If the functions $\varphi_m^{(0)}$ are found with a sufficiently high degree of precision and the number of AO is large, then the solution of the Schroudinger electron equation, can be again

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found, taking into account the electron-electron interactions by the variation method with a function in the form of a linear combination of Slater determinants (the method of superposition configurations), i.e., in the form $\Psi = \sum_i c_i \Phi_i$, in every case for a number of lower electron states. The situation, again reduces to a search for the external values of the quadratic form $\overline{H}_\vartheta = \sum_{ij} c_i c_j H_{ij}$ with elements $H_{ij} = \int \Phi_i \hat{H}_\vartheta \Phi_j \, dq$ on the sphere $S = \sum_i c_i^2 = 1$. It should be noted that the elements $H_{ij} = 0$ when the configurations Φ_i and Φ_j correspond to states with different values of the projections of the total spins for the multielectron system.

Now let us concentrate on one important circumstance. Sup- pose that we have configurations Φ_1, Φ_2, Φ_3 and Φ_4, corresponding to the same spatial state, but with a different distribution of spin components and spin-orbitals.

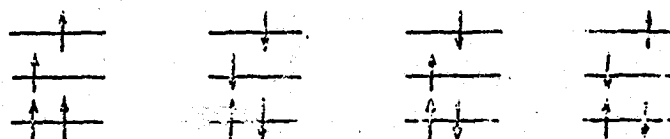This is shown schematically in Fig. 9.

Fig. 9. Scheme of the possible arrangement of four electrons with respect to three energy levels, leading to the appearance of triplet and singlet states.

If we neglect the electron-electron interactions, then all four electron configurations will have the same energy. Four-fold degeneracy occurs. Taking into account this interaction and calculating the elements H_{ij}, we find that $H_{11} = H_{22} \neq 0$, $H_{33} = H_{44} \neq 0$, $H_{12} = H_{13} = H_{14} = H_{23} = H_{24} = 0$ (states with different projections of total spin orbitals) $H_{34} \neq 0$. The eigen-

numbers of the corresponding matrices are $E_1 = H_{11}$, $E_2 = H_{22}$, $E_3 = H_{33} + H_{34}$, and $E_4 = H_{33} - H_{34}$, where $H_{33} + H_{34} = H_{11}$. Thus we have $E_{триил} = E_1 = E_2 = E_3$ (Note: the subscript means "Triplet") and $E_{сингл} = E_4$ (Here the subscript means "singlet"). Consequently, taking account of the electron-electron interaction partially removes the degeneracy of the configurations and leads to the appearance of multiplets (in the given case of a singlet and a triplet). Moreover, it turns out that $E_{синг} > E_{трил} (H_{34} < 0)$, which is a special case of the so-called Gund rule. In the general case the multiplet degeneracy is determined by the formula /26 (2S + 1), where S is the maximum value of the projection of the total spin for the molecule. In the triplet state max S_z = +1 and in the singlet state, S_z = 0.

Real calculations of electron states are not performed with orbital equations with the operator $\hat{H}_э^{(0)}$, but with the so-called self-congruent orbitals which are found by means of the solution of the Schroudinger equation corresponding to the motion of an electron in the field of all the nuclei and the average field of all the electrons. Consideration of this question lies outside the scope of this lecture. We shall only show that each molecular orbital is represented as previously in the form of a LCAO. The use of self-congurent orbitals makes it possible to greatly reduce the number of determinants in their linear combination.

Such is the general scheme for solving numerically the Schroudinger equation in the case of electron motions.

4. The Equation of Vibrations.

The Hamiltonian of the equation for the relative nuclear motions has the form

$$\hat{H}_k = -\frac{\hbar^2}{2} \sum_{k,n} |T|^{1/2} \frac{\partial}{\partial q_k} \frac{\tau_{kn}}{|T|^{1/2}} \frac{\partial}{\partial q_n} + \Delta E_э(Q),$$

where c_{kn} and $|T|$ contain only elements corresponding solely to the deformations of the molecule. The most frequently used generalized coordinates are the changes in the lengths of the bonds, the valence angles and other geometric parameters of a molecule.

The equation with $\hat{H}_k$ has a discrete solution when the potential surface possesses a deep minimum and the motion occurs near it. If the surface does not have a minimum or has a very shallow minimum, then the spectrum obtained is discontinuous. If there is all told one minimum for the potential surface (the case of the basic and near-basic states), then it is possible to expand the potential term in a series with respect to the coordinates.

In a good approximation in very many cases it is possible to limit ourselves just to the quadratic terms in this expansion. Moreover, for small deformations we can assume that the coefficients τ_{kn} and $|T|$ are constant. As a result we obtain an equation which corresponds to the so-called set of harmonic oscillators. Its solution can be obtained by separating the variables through reducing the pair of quadratic forms

$$T_{\kappa u H} = -\frac{\hbar^2}{2} \sum_{k,n} \tau_{kn} \frac{\partial}{\partial Q_k} \left(\frac{\omega}{\partial Q_n} \right)$$

and

$$V_{nOT} = \frac{1}{2} \sum_{k,n} \left(\frac{\partial^2 \Delta E_9}{\partial Q_n \partial Q_k} \right) Q_n Q_k$$

to a sum of squares. As a result, we obtain the sum of the Hamiltonians of the harmonic oscillators.

Then for the energy levels of the entire molecule we have the following simple formula:

$$E_m = \hbar \sum_k \omega_k \left(v_k^{(m)} + \frac{1}{2} \right) , \qquad (16)$$

where $v_k^{(m)}$ are the vibrational quantum numbers, each of which takes on all the values 0, 1, 2, ... and ω_k of the classical normal oscillation frequencies of the system.

Thus each vibrational energy level is described by a set of vibrational quantum numbers, whose number equals the number of vibrational degrees of freedom for the given molecule. If the molecule contains N atoms, then the number of vibrational quantom numbers equals $3N-6$ for non-linear molecules and $3N-5$ for linear molecules. The eigen-functions have the form:

$$\psi_m^{(v)} = \prod_k \psi_k^{(v)'}$$

where $\psi_k^{(v)'}$ are the eigen- functions of the harmonic oscillators.

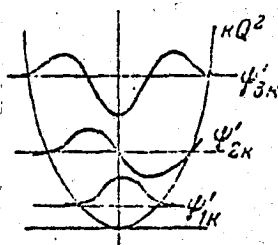The form of certain eigen-functions for a single harmonic /28 oscillator is shown in Fig. 10.

Fig. 10. The form of the eigen-functions of a harmonic oscillator for low energy states.

Eigen-functions have a domain of definition which corresponds approximately to the domain of the possible oscillations of the analogous classical system. For various effects of a molecule, transitions are possible between the vibrational energy levels. It is assumed that they are separated into: basic, or fundamental transitions, to which correspond the transition between

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two energy levels differing from each other by only one quantum number, varying by unity; overtone transitions when one of the quantum numbers changes by more than a unit; and the so-called composite transitions which correspond to changes of two or more quantum numbers by a unit or other number. The scheme of possible transitions for absorption is shown in Fig. 11.
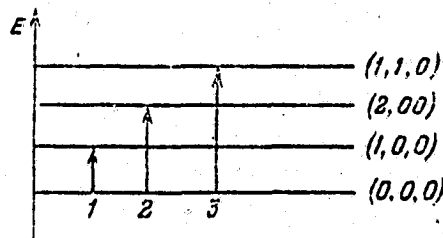

Fig. 11. The scheme of vibrational transitions:

1 - the basic transition; 2 - overtone transition; 3 - composite transition. The quantum numbers are shown in parentheses for the levels when there are three degrees of freedom.

In more complex cases it is necessary to include still higher <u>/29</u> terms of the expansion of the potential energy in a series in terms of the vibrational coordinates, and to express the coefficients τ_{kn} as functions of these coordinates. Thus the so-called <u>kinematic and dynamic anharmonicity</u> appears. This is especially essential in those cases when the molecules are strongly excited or when a transition occurs between two electron states. The transitions which correspond to large vibrational quantom numbers are anharmonic as a rule. In the case of a two-atom molecule the corresponding energy levels can be expressed in the following simple form with a high degree of accuracy

$$E_m = \hbar\,\omega\left(v^{(m)} + \frac{1}{2}\right) - æ\left(v^{(m)} + \frac{1}{2}\right)^2. \tag{17}$$

The coefficient $æ$ is called the anharmonic coefficient. In the case of multiatom molecules such a simple formula cannot be obtained in the general case, and the anharmonic energy levels must be found by numerical methods.

At the present time a number of methods have been developed for solving the anharmonic problem. They can be applied provided that the vibrational quantum numbers are not very large. In attempting to solve the anharmonic problem for oscillations with a very large amplitude we encounter substantial difficulties of a different kind. One of the greatest difficulties is that we have scarcely any information in the case of multiatom molecules concerning the form of the potential surface in the region remote from a minimum.

When the potential surface has two or more minima the solution of the problem is possible provided we are able to find coordinates in the entire set of coordinates for which multiple minima exist. Thus, e.g., for an ammonia molecule it is possible to introduce a coordinate corresponding to the movement of a /30 nitrogen atom over the plane of the atoms of hydrogen such that on the corresponding section of the potential surface there are two minima. In this case the potential is represented approximately in the form:

$$V(Q) = A\,Q^2 + B\,exp\left(-c\,Q^2\right).$$

The solution of the equation with such a potential can be obtained in the form of linear combinations of harmonic wave functions, if in the initial approximation only the term AQ^2 is

retained; the coefficients in these linear combination can be found by the variational method. The energy levels for such a problem are arranged in pairs, and the distance between each doublet is insignificant and decreases from the lowest pair to the highest (inversion doubling). In the case corresponding to the presence of rotational isomers it is possible to introduce so-called coordinates of internal rotation and to solve the corresponding problem with the help of the rotator function with ·supplementary terms which correspond to the periodic potential. The appropriate technique also exists.

Thus in principle it is possible in the most varied cases to investigate the problem corresponding to the relative motions of the nuclei of a molecule.

3. The Equation of Rotations.

The rotational Schroudinger equation contain a Hamiltonian of the general type (10) written in rotational coordinates. The potential part in this equation is absent. An analytic solution is possible only in certain particular cases. Thus, e.g., for rigid, linear molecules and a molecule of the spherical top type (to this type belong molecules with a high degree of symmetry, all three of whose principal moments of inertia I_x, I_y and I_z are equal) the Hamiltonian contains the angular part of the Laplacian written in spherical coordinates. The corresponding /31 eigen-values (energy levels) have the simple form

$$E_{\mathcal{J}} = B\mathcal{J}(\mathcal{J}+1)..$$

(18)

Here B is a constant inversely proportional to the moment of inertia of the molecule $(B \sim \frac{1}{I})$ and T is the rotational quantum number which takes on the values 0, 1, 2, ... An analogous expression for the energy levels can be obtained also for molecules of the symmetric top type $(I_x = I_y \neq I_z).$; however,

for nonsymmetric tops this is impossible and a solution is only possible in numerical form.

It must also be noted that, since a rotating molecule also oscillates, the coefficient B must be assumed to depend on vibrational coordinates, strictly speaking. This results in corrections to formula (10).

The greater the moment of inertia I, the smaller the coefficient B and, therefore, the smaller distance between the rotational energy levels. Consequently in large molecules the rotational structure in the spectrum is unresolved and diffuse, quasicontinuous spectra results.

If all that was said above is taken into consideration, then we obtain the following formula

$$E_{n \upsilon \mathcal{T}} = E_{\vartheta}^{(n)}(0) + \hbar \sum_{k} \omega_{k}^{(n)} \left(\upsilon_{k} + \tfrac{1}{2} \right) + B^{(n)} \mathcal{T}(\mathcal{T}+1). \tag{19}$$

for the energy levels of a molecule in the simplest case.

The superscript "n" refers to the electron states; the subscript "k" enumerates the oscillatory degrees of freedom. The fact that the frequencies of the oscillations $\omega_{k}^{(n)}$ and the coefficient $B^{(n)}$ depend on the electron state of the molecule is taken into account. Strictly speaking, $B^{(n)}$ depends on the oscillatory states also; formula (19) is valid, of course, only for those states whose potential surfaces have sufficiently deep minima such that oscillations are possible and it is possible to speak of definite forms of the molecule. If the potential surfaces have no minima, then we obtain the continuous spectra of the solutions of the Schroudinger equation which cannot be expressed analytically.

4. Selection Rules

Molecules absorb or radiate electromagnetic waves if transitions between energy levels occur. Two important circumstances determine the possibility of such transitions and, consequently, the intensity of the observed lines and bands in the spectra.

The first is connected with the population of the levels. Clearly, transitions from some initial state can occur in principle only if at least part of the molecules of the given set are in this state. Under ordinary conditions the arrangement of molecules according to energy levels is determined by the Boltzmann temperature distribution. However, the inversion population, which is widely used in lazer systems, is possible. Since, as a rule, the number of molecules at high levels is less that at low levels, especially at the basic levels, the radiation spectra are less intense than the absorption spectra.

The second factor is the selection rules. Although none of the selection rules is absolutely rigorous, however, their action is very essential and to a significant degree it characterizes not only the qualitative, but also the quantitative picture of the spectra.

According to the basic quantum mechanical positions the probability of an optical transition between energy levels is given by the square of the matrix element for the operator of the molecular dipole moment, i.e., by the square of an integral of the form:

$$\int \psi'' \hat{\mu} \, \psi' \, dq_v \, .$$

(20) /33

The superscripts indicate the combining states.

Quadripole and more complicated transitions are also possible; however, they are significantly less intense. Therefore we shall limit ourselves to dipole transitions.

In accordance with the three types of movements in a molecule and the three types of spectra, let us consider the probability of transitions for purely electron, vibrational and rotational spectra, and also for electron-vibrational-rotational and vibrational-rotational spectra.

. For purely electron transitions (or transitions between electron states) the following important selection rules hold.

1. Transitions between states with different projections of total electron spins are forbidden (the so-called intercombinational transitions). In particular, singlet-triplet transitions are prohibited. This prohibition is easily derived if we take into consideration the fact that in the Coulomb approximation the spatial and spin parts in the eigen-functions are separated and the orthonormality integral for spin components arises in the expression for the matrix element of the optical transition. The prohibition is lifted when the spin-orbital interactions are taken into account. The prohibition against singlet-triplet transitions leads to the appearance of prolonged luminescence (phosphorescence) in the radiation spectra of multi-atom molecules.

2. Multielectron transitions are prohibited (during a dipole transition it is possible to change the spatial state of only one electron). This rule arises because the matrix element of a dipole moment between two determinant functions of different electron configurations is nonzero only if these configurations /34 differ by at most one spin-orbital. In its turn this is related to the fact that the operator of the electron dipole moment is the sum of single-electron components.

When we convert to more precise expressions for the multi-electron wave function, this prohibition is again lifted and multielectron transitions become possible, although the probability of their occurrence is low.

3. In the case of an optical transition the electron converts from one spin-orbital to another. If these orbitals possess spatial symmetry, which happens in symmetric molecules, then the prohibitions apply with regard to symmetry. Transitions are permitted only between spin-orbitals with a different parity relative to the center of inversion.

4. The following prohibition is related to the presence of a vibrational state in the expression for the total wave function of a multiatom molecule. In the approximation to the total separation of the electron and nuclear motions in the integral (20), a factor of the form

$$\int \psi_k''(Q)\,\psi_k'(Q)\,dQ \qquad (21)$$

is isolated (the superscripts indicate the different combining electron states). It is called the <u>superposition integral</u>.

It is obvious that this integral is zero and the transition is prohibited for those combinations of vibrational levels of combining states where the regions essentially do not overlap in which the functions ψ_k'' and ψ_k' are appreciably different from zero. If the vibrational states correspond to the regions lying inside the potential depressions formed by the respective potential surfaces of the combining electron states, then this condition is satisfied, provided that the minima of the potential surfaces are markedly displaced relative to each other. If two /35 combining states have potential surfaces with sufficiently deep minima and these minima are not greatly shifted with respect to each other, then spectra arise which are either discrete -- when

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a vibrational structure is observed -- or which have an unresolved vibrational structure, but there are absorption bands of finite width. If one of the combining states has a potential surface without minima, then a continuous spectrum is observed.

In the case of electron-vibrational transitions the so-called Franck-Condon principle is closely related to the adiabatic approximation. It states that electron transitions occur in the presence of an unchanged molecular geometry, i.e., so rapidly that the nuclei of the atoms do not succeed in shifting noticeably. We say that the electron transition occurs parallel to the energy axis ("along the vertical") on the diagram of $E_3 = E_3(Q)$, where Q is the set of vibrational coordinates which characterize the deformation of the molecule. Consequently, if in the coordinate space, the extrema of the vibrational functions of a combining electron-vibrational state coincide with the regions in which the vibrational functions of another combining electron-vibrational state are zero, then such a transition is forbidden. This is shown schematically in Fig. 12.
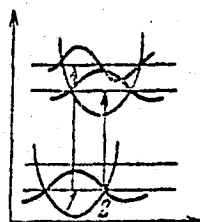

Fig. 12. Schematic representation of the possible electron-vibrational transitions: the transition is permitted (1); prohibited (2).

In order for a transition to be permitted it is necessary that these extrema overlap in at least one region. The greater these overlaps, the greater the probability of the transition.

Therefore, if two potential surfaces of combining states are near each other and differ only by a shift "along the vertical," then the vibrational eigen-functions of these states are also close together, and, thus, due to their orthogonality the integral (21) turns out to be nonzero (the transition is permitted) only for those combinations of vibrationals levels of combining states which have identical sets of vibrational quantum numbers (i.e., $\Delta v = 0$). When the electron-vibrational interactions are partially taken into account, the transitions with $\Delta v = \pm 1$ and even those with $\Delta v = \pm 2$ (but with lower probability) become permissible. If the potential surfaces of electron states differ markedly from each other, then all other transitions also become possible.

When the molecules in combining electron states have symmetry, only those transitions are permitted for which the integrand in (21) is fully symmetric. As we have already shown, the potential surfaces of combining states can be different: they have a different form, minima in different regions of the space of the coordinates Q, etc. As a result, the distribution of the intensities in the vibrational components of the electron bands varies widely. In other words, the contours of the electron-vibrational bands vary within broad limits. The bands can be wide, narrow, symmetric, nonsymmetric, etc. This is demonstrated schematically in Figs. 13 and 14, where for two cases of reciprocally situated potential surfaces (curves) the most probable transitions are shown and the contours of the electron-vibrational absorption bands are obtained.

The vibrational energy levels inside each combining electron state is characterized by a set of corresponding quantum numbers. In the harmonic approximation to the transitions between the vibrational levels of a single electron state the following selec- tion rules hold: only those transitions are permitted for which no more than one quantum number changes by unity. This selection

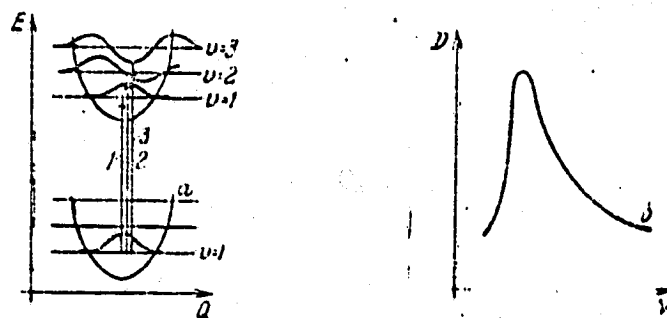Fig. 13. The arrangement of the potential surfaces
and the form of the band contour in the case of a
vertical displacement of the surfaces. The prob-
abilities of transitions are reduced from 1 to 3.
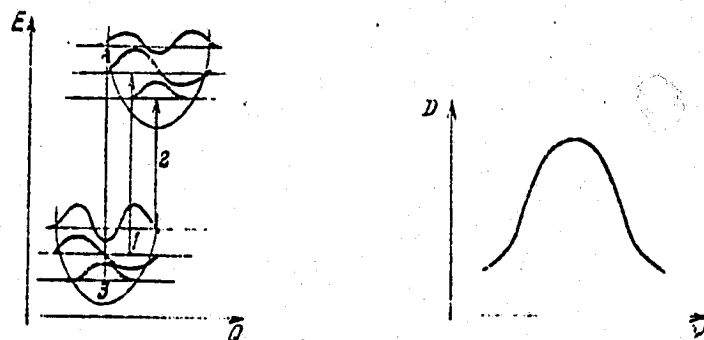Example of an extremely asymmetric band.

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Fig. 14. An example of the formation of a contour
which is almost symmetrical (cf. also the caption
to Fig. 13).

rule is connected with the behavior of the harmonic coscilla-
tion of the eigen-functions with respect to their center (cf.
Fig. 10). Taking anharmonicity into account removes these
restrictions: transitions between levels become possible in
which the quantum numbers vary by more than unity or several
quantum numbers change. The general rule can be formulated as

follows: the greater the difference in the quantum numbers of two combining vibrational states, the lower the probability of the corresponding transition. This rule, together with the familiar reservation, is also applicable to combining states corresponding to different electron levels.

In the vibrational spectrum all transitions are prohibited which correspond to deformations such that the dipole moment of the molecule does not change. In particular this applies to the so-called fully symmetric motions in molecules possessing a center of symmetry. Not all oscillations symmetric relative to this center appear in absorption or radiation spectra.

For the purely rotational spectra only the transitions are permissible for which the changes in the quantum numbers accord with the equation $\Delta \mathcal{T} = \pm 1$; also it is necessary that the molecule possess a nonzero dipole moment in the corresponding electron-vibrational state. There are no dipoleless molecules with a purely rotational spectrum.

If a transition between rotational levels of different vibrational states is completed, but involves one electron state, then the selection rules become complicated. In the spectra the characteristic sets of lines are obtained which are designed as the $R \, (\Delta \mathcal{T} = 1)$, $Q \, (\Delta \mathcal{T} = 0)$, and $P \, (\Delta \mathcal{T} = -1)$ branches. The selection rules for the transitions between the rotational levels of different electron-vibrational states are analogous. It is essential, however, that for different electron states the constants B differ markedly from each other. Since the expression for the difference of the energies of the levels contains linear and quadratic terms relative to T, it can turn out that the quadratic term becomes larger than the linear, which leads to concentration of the lines of one of the branches and to its rotation. We obtain the characteristic sharp boundary of the spectral band -- the edge of the band.

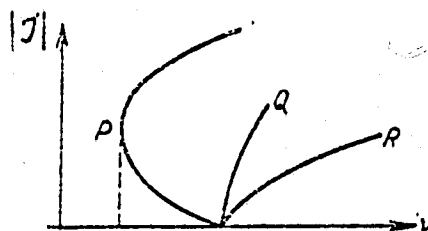The appearance of the P, Q, R branches for this case is shown in Fig. 15.

Fig. 15. The appearance of the frequency branches when $B' > B''$.

The set of prohibition rules mentioned leads to the fact that far from all the transitions between the various energy levels will really appear in the spectrum. As a result the spectrum becomes simpler and more visible.

The selection rules with respect to symmetry are important in particular because the typical picture of the spectra emerging here can be used to identify the membership of a molecule in the appropriate symmetry group.

In conclusion let us again mention that the selection rules shown here are rigorous only when definite assumptions are satisfied: the adiabatic, harmonic hypotheses, the rigid top, etc. In real molecules deviations from these strict rules arise /40 and absorption and radiation bands appear corresponding to the transitions prohibited in the approximation theory. It is necessary to take this into account when interpreting spectra, especially in excited states where many simplifying assumptions turn out not to be satisfied.

5. Computational Possibilities of the Theory of Molecular Spectra.

The contemporary theory of molecular spectra not only makes it possible to clarify the basic mechanisms which are observed in these spectra, but also to carry out numerical calculations comparable with an experiment. These calculations are a basic interpretation of the spectra and indisputably should also play their role in the investigation of objects in outer space.

If we speak of complex molecules, then, with the exception of the calculations of rotational spectra, in all the remaining cases the computational theory is constructed on a semi-empirical basis. Thus, for example, when calculating the vibrational structure the derivatives

$$\left(\frac{\partial^2 E_{\mathfrak{z}}}{\partial Q_k \, \partial Q_n} \right)_0$$

and

$$\left(\frac{\partial^3 \Delta E_{\mathfrak{z}}}{\partial Q_k \, \partial Q_n \, \partial Q_m} \right)_0$$

etc., which are called force constants, are used as semi-empirical parameters. When calculating electron spectra various matrix elements or their components, which correspond to the appropriate variational problem, are introduced as empirical parameters. Similar parameters are sought for some molecules; then they are transferred practically unchanged to other more complex molecules containing the same structural elements. This makes it possible to carry out predictive calculations on the spectra of complex systems. Today such calculations can be performed for the rotational structure of any molecule and the vibrational structures in the basic organic compounds of any degree of complexity, including polymer formations. For electron spectra

basically only the lowest electron states are calculated, but this is done for extremely complex molecules also.

Through the monographs presented in the list of references the reader can acquaint himself with the technique of such calculations.

It is extremely gratifying that for the performance of different types of calculations a significant supply of special programs has been created for domestic electronic computers. In these programs the representation of the input data is so simple that the performance of concrete calculations in many instances is accessible to persons not highly qualified in the theory of molecular spectra.

In conclusion let us add that when observing spectra and comparing them with calculated spectra it is possible with the help of the solution of the inverse spectral problems to obtain a mass of valuable information about the structure and the properties of molecules and ions. This constitutes one of the principal problems of molecular spectroscopy.

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